METHOD AND APPARATUS FOR IMPROVING THE OXIDATIVE THERMAL STABILITY OF DISTILLATE FUEL

The present invention relates to methods of improving the thermal oxidative stability of a distillate fuel, to methods of determining the thermal oxidative stability of a distillate fuel and to apparatus for performing said methods.

Current jet engine fuels have to meet an extensive list of criteria, including
5   corrosion, materials compatibility, freeze point, heat of combustion, conductivity and stability, including storage stability and thermal oxidation stability.

In particular, thermal oxidation stability relates to the stability of the distillate jet fuel at elevated temperatures, such as in the aircraft fuel system and engine. Jet fuels need to meet certain thermal stability specifications to comply with international
10   operational safety requirements.

The current thermal stability specification test method for the most widely used commercial and military aviation jet turbine fuels, ASTM D3241, is based on the Jet Fuel Thermal Oxidation Tester (JFTOT). The JFTOT method is based on measurement of deposition occurring on heated surfaces, and employs a standard electrically heated
15   6061 aluminium tube, typically at 260°C, over the surface of which pre-aerated fuel flows.

Failures in the JFTOT may result from specific deposit coloration on a heated aluminium tube surface or, less frequently, from excessive pressure resulting from the formation of filterable particulates.

20   For a general review of the area of thermal stability see Hazlett, RN. "Thermal Oxidation Stability of Aviation Turbine Fuels", American Society for Testing and Materials, 1991.

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Numerous chemical factors have been linked with the problems of thermal oxidative stability. Although forming only a minor proportion of the fuel, the majority of the deposits formed have been attributed to reactions of relatively minor components present. For example, auto-oxidation has been proposed to be a significant process for

5   deposit formation, and compounds containing oxygen, sulphur, nitrogen and metals have all been linked to the extent of deposit formation.

However, thermal oxidative stability has been shown to vary strongly between different fuels. Although individual components have been identified as contributing to problems of stability in certain fuels in certain situations the previous results have often

10   been contradictory or have been performed under experimental conditions or at temperatures inconsistent with the standard JFTOT test.

It has now been surprisingly found that the majority of deposits formed in the JFTOT test are derived from specific components in the fuel, in the presence of certain metals. In particular, it has been found that the presence of compounds such as indoles

15   and/or pyrroles may be linked to thermal instability of distillate jet fuels and to the formation of deposits in the JFTOT test.

WO 91/05242 relates to a method of testing oil for unstable reactive compounds characterised by contacting at least one said reactive compound from a sample of oil with an acid catalyst to form a coloured reaction product, then relating the visible colour

20   and/or colorimetric absorbance between 600-850 nm of this product to the presence and/or amount of unstable reactive compounds in the oil. According to this publication, it is believed that the test relies upon the oxidation of phenalenes by the oxidising agent to phenalenones and the subsequent formation of coloured indolylphenalene salts in the presence of acid. Such salts are said to be generally blue to blue-violet in colour, but

25   may vary between blue and green in the test.

ASTM standard UOP 276-85 entitled Pyrrole Nitrogen in Petroleum Distillates by Visible Spectroscopy is said to be a method for determining the approximate concentration of pyrroles and indoles having at least one hydrogen per carbon atom in the heterocyclic ring by visible spectroscopy. The method is said to be applicable to

30   gasolines, naphthas, kerosenes and distillate burner oils, but not applicable to crude and vacuum gas oils, which are not completely soluble in *n*-hexane. Olefins are said to interfere with the reaction and must be removed prior to analysis. It is said that

aromatic amines or aliphatic mercaptans can also interfere with the reaction. The method is said to involve removal of olefins by column chromatography followed by addition of 85% phosphoric acid containing p-dimethylaminobenzaldehyde. Acetic acid is added and a deeply coloured red solution is formed. The absorbance of the coloured

5   solution is determined spectroscopically at 540 nm and the result compared to a previously prepared calibration curve, prepared using 2-methylindole as a standard.

This method involves the use of both phosphoric acid and acetic acid as well as chromatographic removal of olefins.

There is thus a need for a method of determining the thermal oxidative stability

10   of a distillate fuel and to apparatus for performing said method, which overcomes or at least mitigates such disadvantages.

Thus, according to a first aspect of the present invention there is provided a method for improving the thermal stability of a distillate fuel which comprises selectively reducing the active concentration in the fuel of N-H containing heterocyclic

15   aromatic compounds in which the nitrogen atom of the N-H group is part of the aromatic system and wherein said fuel also contains an active concentration of metal compounds or will be exposed to active metal compounds in storage or in use.

In addition, as the N-H containing heterocyclic aromatic compounds have been found to cause significant deposits in the JFTOT test in the presence of active metal

20   compounds, it is also possible to improve the thermal stability of the fuel in which both species are present by reducing the active concentration of metal compounds in the fuel.

Thus, according to a second aspect of the present invention there is provided a method for improving the thermal stability of a distillate fuel which comprises reducing the active concentration of metal compounds in the fuel, wherein the fuel also contains a

25   deleterious level of N-H containing heterocyclic aromatic compounds in which the nitrogen atom of the N-H group is part of the aromatic system.

"Deleterious level", as used herein, refers to a level which would have a significant effect on thermal stability as shown by deposit formation on a JFTOT test. Typically, this level will be greater than 20 mg/litre, such as greater than 50mg/litre.

30   According to a third aspect of the present invention there is provided a method for improving the thermal stability of a distillate fuel which comprises selectively reducing the active concentration of N-H containing heterocyclic aromatic compounds in which

the nitrogen atom of the N-H group is part of the aromatic system and reducing the active concentration of metal compounds present in the fuel.

By performing JFTOT tests on model fuels, and analysing the deposits formed using ellipsometry, it has been found that the deposit formation is strongly influenced
5   by the co-presence of both certain metal compounds and certain N-H containing heterocyclic aromatic compounds. In the absence of either component the thermal stability of the fuel is significantly increased.

Relative to these components, certain other compounds, including other nitrogen compounds, sulphur compounds and oxygen compounds have been found to have a
10   relatively smaller effect on deposit formation, regardless of the presence or absence of the metal compounds.

Hence, for a distillate fuel containing both the certain metal compounds and deleterious N-H containing heterocyclic aromatic compounds, the thermal stability of the fuel can be significantly improved by reducing the active concentration of the metal
15   compounds, or alternatively by reducing the active concentration of the N-H containing heterocyclic aromatic compounds, or alternatively by reducing both components.

In particular, and according to the method of the present invention, the thermal stability of the fuel is improved by selectively reducing the active concentration in the fuel of N-H containing heterocyclic aromatic compounds in which the nitrogen atom of
20   the N-H group is part of the aromatic system. By "selectively reducing" as used herein is meant to reduce the active concentration of one or more of the N-H containing species in preference to reducing the concentration of other nitrogen-containing species, and, most preferably, without deliberate reduction of said other species. For example, selectively reducing pyrroles and indoles means to reduce the levels of pyrroles and
25   indoles in preference to other N-containing species, such as pyridines, for example. Hence, non-selective methods of reduction of N-containing compounds, such as hydrotreating, are excluded from the method of the present invention.

Hydrotreating, for example, reduces large numbers of N-containing and other polar compounds in a non-selective manner which can have significant effects on other
30   properties of the fuel, such as the lubricity of the fuel. Selective reduction has the advantage that the overall composition of the fuel is less significantly changed, and hence the other properties of the fuel, such as lubricity are less significantly affected by

the method of the present invention.

In addition, hydrotreating uses a large amount of hydrogen, which has a significant cost. However, as it has now be found that the majority of the deposits formed from a fuel derive from only certain N-containing species, a large amount of this hydrogen is thus utilized removing N-containing species which have relatively insignificant effects in the thermal stability of a fuel.

Hence, selectively reducing the species which have been found to be most deleterious according to the method of the present invention is a more efficient treatment method and avoids or at least mitigates problems with non-selective reduction methods which lead to more significant changes in the composition of the fuel.

The distillate fuel may be a jet fuel, avgas, diesel or gasoline. Preferably, the distillate fuel is a jet fuel, such as Jet-A, Jet A-1, JP-8 or F-35.

The deleterious N-H containing heterocyclic aromatic compounds are those in which the electrons of the nitrogen atom of the N-H group can interact with the aromatic system. Examples of such compounds include pyrrole, indole, pyrazole, carbazole, substituted pyrroles, indoles, pyrazoles and carbazoles, and related compounds, preferably pyrrole, indole, substituted pyrroles and substituted indoles. Such nitrogen atoms, as part of the aromatic system, have a significantly reduced basicity compared to conventional amines. Without wishing to be bound by theory it is believed that this property makes the ring more reactive to coupling and polymerisation type reactions, and hence makes these compounds susceptible to reactions leading to deposit formation.

Certain metals or metal compounds have now been found to contribute to the deposition process. Again without wishing to be bound by theory it is also believed that these metals and metal compounds may catalyse at least a part of the deposition process.

Metals typically present in a distillate fuel may include copper, iron, lead and zinc. Typically these are present at low levels, such as in the parts per billion range (ppb). The active metal compounds which it may be desirable to remove or reduce preferably comprise transition metals and, most preferably, comprise copper and/or iron compounds present in the fuel. Most preferably, the active metal compounds which it may be desirable to remove or reduce comprise copper compounds.

However, even where such metals are not present in the fuel initially or the active

concentration of such metals is otherwise reduced, the fuel may be exposed to active

metals in storage and in use. For example, the US Navy has encountered problems with

copper contamination of JP-5 fuels on aircraft carriers. As a further example, where the

fuel is exposed to steel, such as stainless steel, the fuel may be exposed to any of the

5   transition metals present in the steel and/or these metals may potentially leach in to the

fuel. Hence in cases where the fuel is likely to be exposed to further active metals any

method for the reduction of active metal components at source may not have a

significant effect after storage or in use. Methods that reduce the amount of active

metals, such as copper, to which the fuel is exposed or otherwise prevent the formation

10   of active metal species, are hence preferred.

In general, problems of deposit formation are particularly an issue when the fuel

is at temperature, such as just prior to combustion, for example, in nozzles. However,

where fuel is stored for long periods of time, such as on aircraft carriers, then, although

slower, the degradation of the fuel over time can also be an issue. In addition, the fuel

15   can also be circulated as a coolant prior to use which may increase the extent of

degradation before use.

As described above the methods of the present invention comprise selectively

reducing the active concentration of deleterious N-H containing heterocyclic aromatic

compounds and/or the active concentration of metal compounds present in the fuel.

20   The active concentration of the deleterious N-H containing heterocyclic aromatic

compounds may be selectively reduced by any known method. In one embodiment this

may include physical removal of at least a portion of said compounds from the fuel, for

example by treatment with a suitable adsorbent material. The suitable adsorbent

material is rendered selectively active towards said compounds. Selective adsorption, as

25   distinct from general removal of polar species, will prolong the lifetime of the

adsorption unit by increasing the time for saturation to occur. Selective adsorption may

also increase the ease by which regeneration can be achieved, owing to the specific

nature of the adsorbed species. Selective adsorption may be obtained by surface

modification of common adsorbents to tailor the adsorbent for the specific chemical

30   species, as is known for a range of different applications. For example, selective

adsorption techniques are well known from developments in chromatographic stationary

phase technology and could be readily applied to removal of species according to the

present invention. For example, the relatively low basicity of the deleterious N-H containing heterocyclic aromatic compounds, such as pyrroles, the active concentration of which are to be reduced in the present invention, distinguish them from the more basic compounds also present in the fuel that have found to be less important in the

5   deposit forming process.

Examples of suitable adsorbent material include compounds having a benzaldehyde functionality supported on a suitable support. Preferably, the compound having a benzaldehyde functionality (hereinafter referred to as "benzaldehyde") is a 4-aminobenzaldehyde. It has been found that such compounds will react with pyrroles and

10   indoles to form a complex, thus removing the pyrroles and indoles from the fuel. More preferably, the 4-aminobenzaldehyde is a 4-dialkylaminobenzaldehyde. The alkyl groups of the 4-dialkylaminobenzaldehyde may be the same or may be different. In one embodiment, the alkyl groups are independently selected from methyl, ethyl, propyl and butyl groups. Hence the 4-dialkylaminobenzaldehyde may be, for

15   example, 4-methylethylaminobenzaldehyde, but preferably the alkyl groups are the same, and most preferably the 4-dialkylaminobenzaldehyde is 4-dimethylaminobenzaldehyde.

The suitable support is preferably selected from the group consisting of clays, carbons, aluminas, silicas and zeolites.

20   In an alternative embodiment, the benzaldehyde may be a 4-aminobenzaldehyde functionality which is chemically part of the suitable support, for example, is an end group or pendant group on a polymer backbone that forms the support material.

Preferably, the support is a clay. The suitable adsorbent material is thus, preferably, a surface-modified clay, which clay has been modified by addition of a

25   benzaldehyde. Preferably, the surface-modified clay is prepared by adsorption on to the surface of the clay of the benzaldehyde, more preferably by adsorption of 4-dimethylaminobenzaldehyde. Hence, the clay should exhibit high affinity characteristics for the benzaldehyde, such that the benzaldehyde is strongly, preferably irreversibly, adsorbed.

30   Clays with suitably high affinity for benzaldehydes may be found in a suitable handbook of clay properties, such as the "Data Handbook for Clay Minerals and Other Non-metallic Minerals", edited by H.Van Olphen and J.J. Fripiat, and published by

Pergamon Press.

Preferably, the clay is a kaolinite, more preferably a low defect kaolinite, such as Kaolin KGa-1, available from the Clay Repository of the Clay Minerals Society. Hence, the adsorbent is preferably a low defect kaolinite on which has been adsorbed 4-

5   dimethylaminobenzaldehyde.

Benzaldehydes, in particular 4-dialkylaminobenzaldehydes, have been found to strongly adsorb on the surfaces of kaolinite materials.

The benzaldehyde is preferably adsorbed to a level of at least 0.5 of a monolayer coverage, most preferably to a level of approximately 1 monolayer coverage, such as a

10   coverage equivalent to 0.8 to 1.2 monolayers.

The active concentration of N-H containing heterocyclic aromatic compounds in a fuel may be reduced by contacting said fuel with the suitable adsorbent material in any known manner. This may be done, for example, by mixing the fuel and adsorbent material and subsequently separating the fuel, for example, by filtration. Alternatively,

15   and preferably, the contacting may be achieved by passing the fuel through a suitable column containing the adsorbent material. Any suitable temperature may be used, such as 5 to 100°C, preferably ambient temperature.

The method of the present invention may be performed on the fuel at any suitable stage from, and including at, the refinery, during transportation or in storage of

20   the fuel and up to, including in, the fuel system of the appropriate vehicle. In one embodiment, where the fuel is to be hydrotreated to remove sulphur compounds therein, the method of the present invention may be performed before the fuel is hydrotreated.

In addition, as distinct to adsorbents, specific absorbents derived from size- or shape-selective materials may be used to reduce the active concentration of the

25   deleterious N-H containing heterocyclic aromatic compounds.

Alternatively, or additionally, the reduction of the active concentration of the deleterious N-H containing heterocyclic aromatic compounds may be achieved by reacting the compounds to form species that are inactive or less active in the deposition reaction, for example by complexing the compound (including its participation as a

30   "guest" in a molecular "host-guest" relationship), by addition of a protecting group to the N-H functionality, or by reduction of the reactivity of the compound by substitution of a substituent that makes the aromatic heterocycle less susceptible to deposit forming

reactions.

The active concentration of the metal compounds present in the fuel may also be reduced by any known method. Suitable methods may or may not be molecularly specific in their action. In one embodiment this may include physical removal of at least

5   a portion of said compounds from the fuel, for example by treatment such as ion exchange or by filtration through a suitable adsorbent, such as clay filtration.

Alternatively, or additionally, the reduction of the active concentration of metal compounds may be achieved by reacting the compounds to form insoluble species that may be removed from the fuel or by reacting the metal compounds to form species that

10   are inactive or less active for the deposition reaction, for example by complexing the metal compound or by adding a metal deactivator (MDA) such as a chelating agent, for example disalicylidene-1,2-propandiamine. In one embodiment solid-supported metal chelators can be used whereby selective adsorption of metal species can occur. When used such complexing agents or metal deactivators should be compatible with the

15   intended use of the fuel. In particular, in certain types of fuel, such as in certain jet fuels, it is desired to reduce the number of additives used in the fuel. Hence, it is preferred to reduce the active concentration of N-H containing heterocyclic compounds and not to use metal deactivators to improve the thermal stability of such fuels.

In a further embodiment both deleterious N-H containing heterocyclic aromatic

20   compounds and active metal complexes may be selectively adsorbed by one supported adsorbent system comprising two specific adsorption sites. Where it is desired to reduce the active concentrations of both species this allows effectively simultaneous reduction.

As stated above, thermal oxidative stability has previously been shown to vary strongly between different fuels and results have often been contradictory. Now that it

25   has been found that the deposit formation is strongly influenced by the co-presence of both certain active metal compounds and certain N-H containing heterocyclic aromatic compounds, and that, relative to these components, certain other compounds, including other nitrogen compounds, sulphur compounds and oxygen compounds have been found to have a relatively smaller effect on deposit formation, it is possible to explain at

30   least some of the previous variation in thermal oxidative stability results between different fuels and by different groups.

It is also now possible to devise improved testing methods for determining the

thermal oxidative stability of a distillate fuel.

Thus, according to a fourth aspect of the present invention there is provided a test method for determining the thermal stability of a distillate fuel, which test method comprises (a) contacting the distillate fuel with a solvent being at least partially

5   immiscible with said fuel and comprising 4-aminobenzaldehyde in formic acid, to form an oil-immiscible layer and (b) relating the visible colour and/or colorimetric absorbance between 400 and 700 nm of said oil-immiscible layer to the thermal stability of the fuel.

Preferably, the 4-aminobenzaldehyde is a 4-dialkylaminobenzaldehyde.

10   The alkyl groups of the 4-dialkylaminobenzaldehyde may be the same or may be different. Suitably, the alkyl groups are independently selected from methyl, ethyl, propyl and butyl groups. Hence the 4-dialkylaminobenzaldehyde may be, for example, 4-methylethylaminobenzaldehyde. More preferably the alkyl groups are the same, and most preferably the 4-dialkylaminobenzaldehyde is 4-dimethylaminobenzaldehyde.

15   The test method of the present invention solves the technical problem identified with prior art testing methods above, not least by providing a test which does not require the prior removal of olefins. In addition, the test method takes advantage of the immiscibility of formic acid with the fuel, its ability to partition the active pyrrolic and indolic compounds from the fuel, and its relatively weak acidity, such that the procedure

20   uses fewer reagents and operations, and avoids the necessity of separating the indoles by column chromatography.

The colour and/or colorimetric absorbance may be related to thermal stability of the fuel by a suitable comparison. For example, the visible colour of the oil immiscible layer may be compared, by eye, with a suitable reference colour chart. Alternatively, the

25   colorimetric absorbance between 400 and 700nm may be measured using a suitable spectrometer to give measured absorption values at one or more values or over one or more ranges within the range 400 to 700 nm, and this value may then be compared with suitable reference data, such as absorbance values for suitable reference fuels. The reference data may be in the form of a graph of absorbance versus concentration of

30   particular components or may relate the absorbance directly to the thermal stability of the distillate fuel.

The reference fuels may be solutions comprising known concentrations of model

compounds, such as indole or 2-methylindole, in hydrocarbon model fuels, such as, for example, dodecane.

The test method of the present invention may be applied to jet fuel, avgas, diesel or gasoline distillate fuels.

The solvent is preferably a solution of the 4-aminobenzaldehyde in formic acid but may also comprise water, for example, a solution of 4-aminobenzaldehyde in aqueous formic acid, or mixtures with other oil-immiscible liquids.

The concentration of formic acid in the solvent may be at least 20% by weight, preferably at least 50% by weight.

The concentration of 4-aminobenzaldehyde in the solvent may be in the range 500 to 5000 mg/l, preferably 2000 to 3000 mg/l . Preferably, the 4-aminobenzaldehyde is 4-dimethylaminobenzaldehyde, which is a commercially available compound sometimes referred to as Ehrlich's reagent.

The test method of the present invention can be preformed using on relatively small amounts of fuel, and using relatively small amount of solvent.

Hence, the amount of distillate fuel used in the test method of the present invention may be in the range 2 to 25 ml, preferably in the range 5 to 10 ml.

The amount of solvent should be sufficient for the colour and/or colorimetric comparison, for example for colorimetric analysis, typically at least 5ml, preferably in the range 5 to 25 ml, more preferably in the range 5 to 10 ml

The fuel may be contacted with the solvent, preferably by mixing under agitation, such as stirring or shaking, and suitably at ambient temperature. Suitable mixing may be achieved in 5 seconds or less, but preferably mixing may be for at least 10 seconds, such as 10 to 30 seconds. Generally, shaking for 10 to 20 seconds is sufficient to achieve mixing.

The fuel and solvent are then allowed to separate, typically for a period of at least 5 minutes, such as 5 to 30 minutes, preferably 10 to 20 minutes.

Also, according to the present invention there is provided an apparatus comprising a kit of parts suitable for use in the test method of the present invention.

In one embodiment, said apparatus comprises a first vessel containing a determined amount of solvent comprising a determined amount of 4-aminobenzaldehyde in formic acid, a measuring container suitable for measuring a

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determined amount of the distillate fuel, a second vessel suitable for mixing the determined amount of solvent with the determined amount of distillate fuel, and a third vessel suitable for optical analysis of the solvent phase.

Preferably, the 4-aminobenzaldehyde is a 4-dialkylaminobenzaldehyde.

5   The alkyl groups of the 4-dialkylaminobenzaldehyde may be the same or may be different. Suitably, the alkyl groups are independently selected from methyl, ethyl, propyl and butyl groups. Hence the 4-dialkylaminobenzaldehyde may be, for example, 4-methylethylaminobenzaldehyde. More preferably, the alkyl groups are the same, and most preferably the 4-dialkylaminobenzaldehyde is 4-dimethylaminobenzaldehyde.

10   Alternatively, two or more of the first to third vessels described in the first embodiment of the apparatus may be replaced by a single vessel. For example, the first vessel containing a determined amount of solvent may also be suitable for mixing of the determined amount of solvent with the determined amount of distillate fuel, and/or may also be suitable for optical analysis of the solvent phase.

15   As a further, preferable, example, the vessel suitable for mixing the determined amount of solvent with the determined amount of distillate fuel is also suitable for the subsequent optical analysis of the solvent phase. In this preferred embodiment, the first vessel preferably comprises a vial containing a specific volume of the solvent comprising a determined concentration of 4-aminobenzaldehyde in formic acid – for

20   example 5ml of solvent containing 3mg of 4-dimethylaminobenzaldehyde per ml of formic acid. The preferred apparatus also comprises a measuring container, such as a measuring cylinder or a suitable pipette for measuring the required amount of distillate fuel, and a stoppered container for mixing the fuel and solvent, said container also being suitable for subsequent optical analysis. For example, the stoppered container may be a

25   stoppered cuvette suitable for mixing the fuel and solvent, which cuvette, after allowing the phases to separate and being placed in a suitable measurement device, allows the solvent phase to be directly analysed. The suitable measurement device may be a colour comparator or may comprise a more sophisticated spectrophotometer which may measure absorbance at one or more specific wavelengths and/or over a given

30   wavelength range (for example, by integration), such as, especially where the 4-aminobenzaldhyde is 4-dimethylaminobenzaldehyde, the range 530 to 570nm.

In addition to the improved test method described above, the present invention

also allows improvements to be made in the JFTOT test. Hence, it is now possible to calibrate or otherwise verify the performance of JFTOT or other thermal oxidative stability testing apparatus using one or more calibration fluids (standards) comprising the active metal compounds and/or active N-H containing heterocyclic aromatic

5   compounds, said compounds being as defined above. This calibration allows the user of the apparatus to plot the response of the JFTOT or other thermal oxidative stability apparatus to said compounds, and hence to identify the contribution of said compounds to the deposits formed in JFTOT or thermal oxidative stability tests.

Therefore, the present invention also provides one or more calibration fluids

10   comprising a known concentration of active N-H containing heterocyclic aromatic compounds and/or a known concentration of active metal compounds, and a hydrocarbon phase.

The present invention also provides a method of calibration of a thermal oxidative stability apparatus using one or more calibration fluids comprising a known

15   concentration of active N-H containing heterocyclic aromatic compounds and/or a known concentration of active metal compounds, and a hydrocarbon phase.

The active N-H containing heterocyclic aromatic compounds and/or active metal compounds are as described above. The thermal oxidative stability apparatus is preferably a JFTOT apparatus. The hydrocarbon phase may be any suitable hydrocarbon

20   or mixture of hydrocarbons of known composition. Preferably, the hydrocarbon phase is a saturated aliphatic hydrocarbon of 8 to 15 carbons atoms, for example, n-dodecane.

The one or more calibration fluids preferably comprise one or more fluids containing both active N-H containing heterocyclic aromatic compounds and active metal compounds, but may also comprise one or more fluids containing active N-H

25   containing heterocyclic aromatic compounds but not containing active metal compounds and/or one or more fluids containing active metal compounds but not containing active N-H containing heterocyclic aromatic compounds.

In one embodiment a single calibration fluid may be used to produce a deposit in the thermal oxidative stability apparatus, such as in a JFTOT tube. In another

30   embodiment, more than one calibration fluid is used, and the calibration fluids may be used to produce more than one deposit, such as a series of deposits, in the thermal oxidative stability apparatus, for example a series of deposits in JFTOT tubes with

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varying deposit colouration.

Such deposits may be used as standard responses (standards) and allow the results from unknown fuels to be compared. Where enough standards are known a calibration curve may be derived.

In addition to measuring unknown fuels on an apparatus, results on fuels from different thermal oxidative stability equipment can be readily compared using the results from equivalent standards run on the respective pieces of equipment.

The deposits formed from a calibration fluid according to the present invention may also be used to verify the performance of a thermal oxidative stability apparatus, for example, to check that the apparatus is performing within acceptable ranges and/or with required reproducibility/accuracy. Hence calibration fluids as used herein includes verification fluids comprising the active metal compounds and/or active N-H containing heterocyclic aromatic compounds, and the method of calibration according to the present invention includes verification of the performance of the thermal oxidative stability apparatus using one or more verification fluids.

The calibration fluids may be run individually to create such standards and/or may be mixed with other such calibration fluids and/or with fuels. For example, the mixture of two calibration fluids in a known combination will give a third calibration fluid of known composition. Alternatively an unknown fuel may be combined (or doped) with a known quantity of a calibration fluid, and the results from the doped fuel compared to the undoped fuel (and, optionally, with standards).

The calibration fluids preferably have an active N-H containing heterocyclic aromatic compound content, for example 2-methylindole, pyrrole and/or 2,5-dimethylpyrrole content, of from 0 to 250mg/l. The calibration fluids preferably have an active metal compounds content, for example a copper(II) ion content, of from 0 to 100ppb.

In a similar manner to their use to produce deposits in a JFTOT apparatus, the calibration fluids may also be used as calibration fluids for other types of thermal oxidative stability tests, such as the test method of the fourth aspect of the present invention.

The invention will now be illustrated by reference to following examples and Figures 1 to 11.

Figure 1 shows results from JFTOT screening of different compounds in Jet A-1
(J1) at 270 and 280°C on aluminium JFTOT tubes.

Figure 2 shows a comparison between deposition tendencies for J1 jet fuel and
dodecane containing 250 mg l^{-1} 2-methylindole as a function of JFTOT test

5   temperature.

Figure 3 shows JFTOT tube profiles showing the effect of different copper (II)
concentrations in dodecane on deposit formation in the presence of 250 mg l^{-1} 2-
methylindole at 260°C.

Figure 4 shows aluminium JFTOT tube profiles showing the deposition occurring

10   in dodecane containing 100 ppb Cu^{II} and 250 mg l^{-1} thianaphthene at 260 and 340°C.

Figure 5 shows aluminium JFTOT tube profiles showing the deposition occurring
in dodecane containing different concentrations (indicated) of collidine and copper(II) at
260°C.

Figure 6 shows the dependence of JFTOT deposit volume on copper(II)

15   concentration in the presence of pyrrole and 2,5-dimethylpyrrole using aluminium tubes
at 260°C.

Figure 7 shows the effect of a metal deactivator (6 mg l^{-1}) on deposition produced
from dodecane in the 2-methylindole (250 mg l^{-1}) / 100 ppb copper(II) system
(aluminium tubes).

20   Figure 8 shows stainless steel JFTOT tube deposit profiles showing the deposition
occurring in dodecane containing 2-methylindole (250 mgl^{-1}) and different copper(II)
concentrations at 260°C.

Figure 9 shows the effect of a metal deactivator on deposition produced from
dodecane in the 2-methylindole (250 mg l^{-1}) / 100 ppb copper(II) system (stainless steel

25   tubes).

Figure 10 shows a calibration plot showing absorbance at 545 nm of formic
acid/DMAB solutions as a function of 2-methylindole concentration in dodecane.

Figure 11 shows the UV-Visible spectra for formic acid/DMAB solutions of
extracts from three jet fuels.

30   <u>EXAMPLES</u>

<u>Materials</u>

n-Dodecane (ex Aldrich) was used as the model hydrocarbon phase for the

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JFTOT studies. Samples of a jet fuel (Jet A-1, ex Coryton Refinery) with a breakpoint of 270°C were also used in several of the tests.

The following compounds were used as dopants in the typical ranges expected for such compounds in real fuels: pyrrole, 2,5-dimethylpyrrole, indole, 2-methylindole, 3-
5   methylindole, 2-methylindoline, 2,4,6-trimethylpyridine, 3-methylquinoline, thianaphthene, benzofuran and indene.

Methods

JFTOT tests were conducted, unless stated otherwise, under standard ASTM D3241 conditions, although temperature was varied in some tests. Standard 6061
10   aluminium and 316 stainless steel tubes were purchased from the manufacturer, Alcor. Deposition levels were quantified using an ellipsometric technique as described in C Baker, P David, S E Taylor and A J Woodward, *Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels*, Rotterdam, 433-447 (1995) which is herein incorporated by reference. Deposit thickness measurements were made
15   over the tube surface at regular intervals using a Philips "Fuel Qualifier" instrument, and the deposit volumes determined by integrating the thickness results. This approach was applied to both types of tube, after inputting the pre-determined baseline parameters for aluminium and stainless steel.

Deposition on Aluminium JFTOT Tubes and Identification of Deleterious Species

20   2-Methylindole, thianaphthene (benzothiophene), benzofuran and indene, which are characteristic of some of the polar and olefinic components of distillate (including jet) fuels, were dosed at concentrations up to 250 mg l^{-1} to a sample batch of Jet A-1 fuel (J1), and the JFTOT test run at temperatures up to 280°C.

The results are shown in Figure 1. It is evident from the results of this initial
25   screening that the most significant deposition occurs in the presence of 2-methylindole at the test temperatures of 270 and 280°C.

Additional screening was carried out using dodecane dosed with the same compounds at concentrations up to 500 mg l^{-1} and temperatures up to 340°C. In this case there was little evidence of deposit formation for any of the compounds tested.
30   Figure 2 shows the data for 2-methylindole, which exhibited the highest deposit-forming tendency when tested in J1.

Copper (II) naphthenate was then added at varying concentrations to the dodecane

in the presence of 250 mg l^{-1} 2-methylindole, and the JFTOT test performed at 260°C. The results are shown in Figure 3. The deposits in the presence of copper bore a strong resemblance to those generated from J1.

These results demonstrate that significant deposit formation from the model fuel requires the presence of both an active concentration of the N-H containing heterocyclic aromatic compound and an active concentration of the metal compound.

Thianaphthene, benzofuran and indene were also tested in an identical manner. However these substrates all showed low deposit volumes with no significant change in the deposition tendencies for these substrates in the presence of copper, compared with its absence. These results show that these non-N-H containing aromatic compounds do not give significant deposit formation. Figure 4 shows this for dodecane containing 100 ppb copper(II) and 250 mg l^{-1} of thianaphthene at two temperatures.

Further nitrogen-containing substrates (derivatives of quinoline, pyrrole and pyridine) were then tested in the same manner.

Figure 5 shows the effect of different concentrations of collidine (2,4,6-trimethylpyridine) and copper(II) on deposit formation from dodecane on aluminium at 260°C. The deposit formation was seen to be relatively low. The same effect was found for 3-methylquinoline. This behaviour was also found to be consistent with its behaviour in J1 fuel. These results show that these non-N-H containing aromatic compounds do not give significant deposit formation (they are N-containing aromatic heterocycles, but not N-H containing).

Pyrrole and 2,5-dimethylpyrrole were also tested. The results are shown in figure 6. Both pyrrole and 2,5-dimethylpyrrole produced significant levels of deposits, but it is evident that 2,5-dimethylpyrrole produced a greater level of deposits than pyrrole itself. As the data in Figure 6 shows, the deposits from the dimethyl- derivative become too thick for the ellipsometric technique to measure reliably.

These compounds are both N-H containing heterocyclic aromatic compounds according to the invention. The data in Figure 6 shows that such compounds, in the presence of an active concentration of metal compounds produce significant deposits.

Figure 7 shows the effect of addition of a metal deactivator (disalicylidene-1,2-propandiamine), in the case of the 2-methylindole system. It can be seen from Figure 7 that the use of a metal deactivator reduces the formation of deposits. Figure 7 thus

illustrates a method of improving the thermal stability of the fuel (reducing deposit formation) by reducing the active concentration of metal compounds in the fuel, according to one aspect of this invention.

Deposition on Stainless Steel JFTOT Tubes

5   The following experiments were performed using stainless steel JFTOT tubes.

Figure 8 contains deposit profiles for JFTOT tests carried out on 2-methylindole (250 mgl^{-1}) in the presence different copper(II) concentrations. It can be seen that the deposit formation is less dependent on the presence of copper on stainless steel than found for aluminium tubes in Figure 3, and deposits are seen even in the absence of

10   added copper for 2-methylindole. The total deposit levels with 100ppb copper in dodecane containing 2-methylindole (250 mgl^{-1}) are similar on both aluminium tubes and stainless steel tubes under these conditions.

Deposits from thianaphthene in the absence of added copper however were still low and comparable to the deposits seen on aluminium tubes.

15   These results illustrate that the presence of active metal compounds may be due to the metallurgy with which the fuel is in contact. Even in the absence of added copper (or other metal) compounds, active metal compounds are present when using a stainless steel JFTOT tube.

These results also further illustrate that the presence of a deleterious N-H

20   containing heterocyclic aromatic compound is still required for significant deposit formation.

Figure 9 shows the effect of addition of a metal deactivator (disalicylidene-1,2-propanediamine), in the case of the 2-methylindole system on stainless steel. Again the use of a metal deactivator reduces the formation of deposits.

25   These results illustrate that the use of a metal deactivator will still reduce the active concentration of metal compounds when these are due to the metallurgy with which the fuel is in contact.

Use of model solution to produce standard responses

The following examples illustrates the production of a calibration fluid

30   comprising active N-H containing heterocyclic aromatic compounds and/or active metal compounds, and the use of such a fluid to calibrate a thermal oxidative stability apparatus. The method of preparation of the calibration fluid is similar to that used to

prepare the solutions described in the Examples above.

The following reagents, of 98%+ purity, were used as-received:

n-Dodecane "99%+" ex Aldrich

2-Methylindole "98%" ex Aldrich

5   Copper(II) naphthenate ex Strem Chemicals.

600 ml of the n-dodecane was measured into a 1-litre measuring cylinder. 150 mg of 2-methylindole was dissolved, with mild sonication, in approximately 0.5 ml AnalaR toluene, and the resultant solution was added to the dodecane in its entirety to give a dodecane solution containing 250 mg/l of 2-methylindole.

10   Separately, a stock solution of copper naphthenate (CN, approx. 8% copper) was prepared by dissolving, again with mild sonication, an accurately weighed amount of approximately 10mg CN in 10 ml AnalaR methanol. Copper assay data was obtained for the CN, so that the volume of this stock solution required to produce a 50 ppb copper solution could be calculated, and this volume was added, using a microlitre

15   syringe, to the dodecane / 2-methylindole solution to give a calibration fluid comprising 250mg/l of 2-methylindole and 50ppb copper (II). Other hydrocarbon-soluble copper compounds of known copper content could be used instead of CN in this procedure.

The resultant mixture was then be subjected to testing in a JFTOT under ASTM D3241 conditions at 260°C.

20   The deposit thus formed may be used as a standard and compared to deposits obtained from jet fuels in the same apparatus or may be used to verify the performance of the apparatus.

The volume of deposit resulting from this test using the calibration fluid as described above should be in the range 1 to 2 x 10^{-5} cm^3, corresponding approximately

25   to a "3" visual colour rating on the ASTM D3241 scale.

Further calibration fluids, with different concentrations of active N-H containing heterocyclic aromatic compounds and/or active metal compounds may also be prepared by a similar method and used to give further standards.

As an example of a method of calibration of a JFTOT using a series of calibration

30   fluids, Figure 3 shows a series of deposits formed at varying concentrations of copper (II) compounds in a model fuel with 250mg/l of 2-methyindole. These could form a series of standard deposits, as described above, for the particular JFTOT apparatus and

conditions. An unknown fuel could be tested on the same apparatus and under the same conditions and compared to these deposit profiles. The calibration data could be used to derive the level of deposit forming compounds in the fuel.

Additionally one or more calibration fluids equivalent to the calibration fluids

5 used to generate the standard deposits could be run in the JFTOT to form further deposits, which can be compared to the standard deposits expected to verify the performance of the JFTOT apparatus is as expected.

Figure 8 shows a similar series of deposits formed under different conditions (in this case with a different JFTOT tube), which could be used to compare an unknown

10 fuel tested under these different conditions.

In addition comparison of the responses of equivalent standards measured under the different conditions, e.g. the 50ppb and 100ppb copper(II) traces in Figures 3 and 8 would allow different fuels run under the different conditions to be compared. This would equally apply to experiments on different sets of apparatus.

15 Test method of the present invention

Three jet fuels with different thermal stabilities, as determined using the Jet Fuel Thermal Oxidation Tester (JFTOT), were examined using the test method of the present invention by adding 5ml of a formic acid solution containing 3mg of 4-dimethylaminobenzaldehyde (DMAB) per ml of formic acid to 5ml of fuel, shaking for

20 20 seconds and allowing to separate for 20 minutes. Previously, a calibration plot was constructed using different concentrations of 2-methylindole (Aldrich) in dodecane as fuels. This calibration is shown in Figure 10 to be linear in the 2-methylindole concentration range 0-25 mg/l typical of concentrations expected in jet fuels. The absorbance values were corrected for the absorbance of the original formic acid/DMAB

25 solution over the wavelength range being considered.

The jet fuels were treated in the same manner, and their UV-Visible spectra determined using a Cary 50 spectrophotometer. The absorbance at 545 nm was used to determine the concentration of indoles in the sample (expressed as "2-methylindole equivalent concentration"). Figure 11 shows the UV-Visible spectra for the three jet

30 fuels. From these absorbance data, the equivalent indole concentrations given in Table 1 are obtained. Two different methods, giving the same relative results are compared in Table 1. In the first, the absorbance readings at a single wavelength (545 nm) are

compared with the standard values for 2-methylindole. Other indoles could be selected

for this comparison. In the second example of possible comparisons, an integrated

absorption intensity is selected as a criterion, opening up the possibility that substituent

effect in the indole structure may change the position of maximum absorption. A

5   calibration, equivalent to that given in Figure 10, but for indole itself, leads to the

analysed data in Table 1, columns 4 and 6.

The differences between the two sets of "equivalent data" are to be expected,

since the fuels will contains different substitution patterns on the indole ring. The data

indicate that low indole levels favour lower JFTOT tube ratings, although other failure

10   mechanisms (*e.g.* pressure failures) may not always be predicted, owing to the

complexity of reactions occurring during thermal stressing of fuels – for example, see S

E Taylor, ACS Petroleum Chemistry Division Preprints, 2002, 47(3), 166.

Table 1

Jet Fuel Data

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Fuel reference number	JFTOT visual rating (ASTM D3241 at 260°C)	Absorbance at 545 nm	Integral absorbance between 500 -600nm $(= \int_{500}^{600} A.d\lambda)$	2-Methylindole equivalent concentration (2MIEC; mg/l) from A_{545nm}*	Indole equivalent concentration (IEC; mg/l) from $\int_{500}^{600} A.d\lambda$ **
B02/166	<3	1.468	117.4	11.4	3.42
B02/218	2A (also ΔP >25 mmHg)	0.25	27.6	1.9	0.80
B02/062	1	0.106	9.1	0.8_2	0.27

*$A_{545nm} = 0.129 C_{2\text{-Methylindole}}$

**$\int_{500}^{600} A.d\lambda = 34.3 C_{Indole}$

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